

DIRECT COMPARISON OF XAFS SPECTROSCOPY AND SEQUENTIAL EXTRACTION FOR ARSENIC SPECIATION IN COAL

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ABSTRACT

The speciation of arsenic in an Ohio bituminous coal and a North Dakota lignite has been examined by the complementary methods of arsenic XAFS spectroscopy and sequential extraction by aqueous solutions of ammonium acetate, HCl, HF, and HNO₃. In order to facilitate a more direct comparison of the two methods, the arsenic XAFS spectra were obtained from aliquots of the coal prepared after each stage of the leaching procedure. For the aliquots, approximately linear correlations ($r^2 > 0.98$ for the Ohio coal, > 0.90 for the ND lignite) were observed between the height of the edge-step in the XAFS analysis and the concentration of arsenic measured by instrumental neutron activation analysis. Results from the leaching sequence indicate that there are two major arsenic forms present in both coals; one is removed by leaching with HCl and the other by HNO₃. Whereas the XAFS spectral signatures of the arsenic leached by HCl are compatible with arsenate for both coals, the arsenic leached by HNO₃ is identified as arsenic associated with pyrite for the Ohio coal and as an As³⁺ species for the North Dakota lignite. Minor arsenate forms persist in both coals after the final leaching with nitric acid. The arsenate forms extracted in HCl are believed to be oxidation products derived from the other major arsenic forms upon exposure of the pulverized coals to air.

INTRODUCTION

The techniques of sequential leaching and XAFS spectroscopy have both been used to determine modes of occurrence of elements in coal. Both methods have their advantages and disadvantages. XAFS spectroscopy is a direct probe of the occurrence of elements and is capable of providing information on how specific elements exist in coal at concentrations as low as 2 ppm. The major disadvantage of the technique is that only a single spectrum is obtained which is the weighted sum of all the occurrences of the element in the coal. This problem can be largely avoided by examination of different fractions of the coal separated by various physical methods, such as float/sink in heavy liquids or froth flotation [1,2]. In addition, a database of possible occurrences of the element in coal must also be established for comparative purposes [2,3]. Finally, the method is limited to a single element at a time. Sequential leaching is an indirect method and is based upon the anticipated behavior of certain mineral types in a suite of progressively stronger acidic reagents. It has the advantage that it is a multi-element technique, although depending on the analysis methods used to determine the concentrations of the elements in the residues and solutions, the analysis time can be lengthy. As with any indirect method, sequential leaching is only as good as the assumptions on which it is based and the technique may be completely misleading if the assumptions are incorrect.

In this study, we present the first direct comparison of XAFS and sequential leaching methods for determination of elemental modes of occurrence in coal. Data from both methods are presented for the speciation of arsenic in two different coals: a bituminous coal from Ohio and a lignite from North Dakota.

EXPERIMENTAL

(i) Coals Investigated

Three coals were initially considered for this study: a bituminous coal from Ohio, which is a blend of coal mined from the Ohio No. 5, 6 and 7 seams, a subbituminous coal from the Wyodak seam in Wyoming, and a lignite mined from the Hagel seam in North Dakota. All three coals are used for electrical power generation at full-scale utility operations and the samplings are representative of the coal, in both composition and particle-size (~70% -200 mesh), fed to the burners at the power plants.

The trace-element contents of the two coals were determined by a combination of instrumental neutron activation analysis (INAA), inductively-coupled plasma mass spectrometry (ICP-MS), and ICP atomic emission spectroscopy (ICP-AES). Arsenic contents determined for the Ohio bituminous coal, the North Dakota lignite and the Wyodak subbituminous coal are 18, 10, and 1.7 ppm (dry basis), respectively. Owing to its very low arsenic content, the Wyodak coal was not investigated in the detail afforded to the other two coals.

(ii) Sequential Leaching Procedure

Preparation of the coal samples and the sequential extraction analysis were performed at the U.S. Geological Survey at Reston. The procedure is described in detail elsewhere [4,5]. It consists of the following sequence of extractions: (1) 1N ammonium acetate, (2) 3N HCl, (3) 48% HF, and (4) 2N HNO₃. Each extraction is performed in 50 ml centrifuge tubes on a wrist-shaker, except for the extraction in HNO₃, which is performed in 125 ml Erlenmeyer flasks [5]. These extractions are designed respectively to solubilize (1) exchangeable cations and some readily soluble carbonate species, (2) more resistant carbonates and simple sulfides (ZnS, PbS, CuFeS₂), (3) clays and other silicates, and (4) iron disulfides (pyrite and marcasite, FeS₂). After each stage, the concentrations of elements in the extract were analyzed using ICP-AES and ICP-MS and portions of the residue were saved for analysis using INAA and CVAA and also for XAFS spectroscopy.

(iii) Arsenic XAFS spectroscopy

Arsenic K-edge XAFS spectroscopy was carried out at beam-line X-18B at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, NY, during a period when the synchrotron was operated in maximum flux mode at 2.8 GeV with currents up to 400 mA. Arsenic XAFS spectra were collected in fluorescent mode using a 12-element germanium array detector [6]. The coal residue samples were suspended in the monochromatic X-ray beam by means of ultra-thin polypropylene bags. In addition to multiple scanning, both Soller slits and a 6μ Ge filter were employed to enhance the signal/noise ratio of the spectra as much as possible. XAFS spectra were typically collected at X-ray energies ranging from about 100 eV below to at least 500 eV above the arsenic K absorption edge using a rotating Si (220) double crystal monochromator to select the energy. A thin smear of As₂O₃ on scotch tape was used as the primary calibration standard; this sample was run in an absorption experiment after the fluorescence experiment so that it provided a simultaneous calibration. The major peak in the absorption spectrum of As₂O₃ was used to define the zero-point of energy for the arsenic XAFS spectra. It is assumed to occur at 11,867 eV.

The XAFS data collected at the synchrotron were returned to the University of Kentucky for analysis. The data were analyzed in the usual fashion [7,8]: after calibration of the energy scale, the spectra were split into separate X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regions and each region was analyzed independently. The XANES region was used not only as a fingerprint for identification of the forms of occurrence of arsenic in the fly-ash samples, but also as the basis for extracting percentages of the different arsenic forms present in the coal sample. This was achieved by means of a calibrated least-squares analysis routine developed for analysis of arsenic XANES spectra [9], an example of which is shown in Figure 1. Owing to the low arsenic contents of the coal samples, neither the EXAFS region nor the radial structure function (RSF), which is derived from the EXAFS spectrum by mathematical manipulation [7,8], was useful for this study.

RESULTS AND DISCUSSION

(i) Sequential Leaching

Results from the sequential leaching will be reported in detail elsewhere; here, data will be presented and discussed only for arsenic. The arsenic contents of the residue fractions, determined by instrumental neutron activation analysis (INAA) after each extraction, are summarized in Table 1:

Table 1: As contents of residues remaining after leaching experiments

	Ohio bituminous As in ppm	Wyodak subbit. As in ppm	N. D. lignite As in ppm
After Amm. Acet. leach	19.1	1.7	11.0
After HCl leach	15.1	1.0	5.2
After HF leach	15.2	0.7	3.6
After HNO ₃ leach	0.9	0.4	1.6

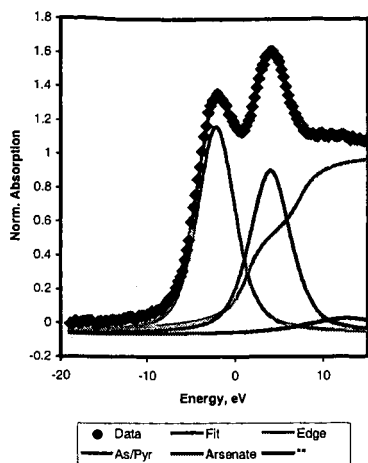


Figure 1: Least-squares fitted As XANES spectrum of Ohio bituminous coal after the ammonium acetate leach.

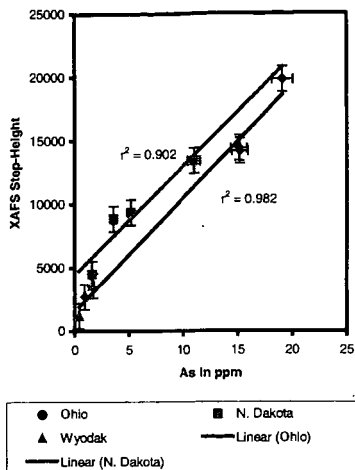
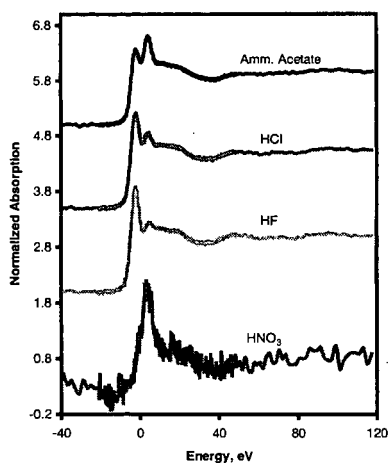
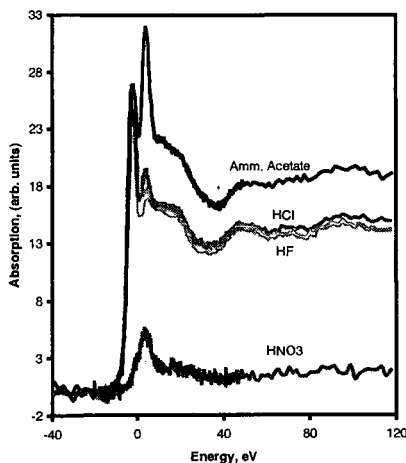


Figure 2: Correlation between the XAFS step-height and the concentration of arsenic in the leached residues.

The analytical data in Table 1 can be correlated with the step-height determined from XAFS spectra, which is also an approximate measure of the arsenic concentration. This correlation is shown in Figure 2. The correlations between the analytical data and the XAFS edge-step heights for the two coals show a reasonable approximation to a linear relationship. For the Ohio bituminous coal, the correlation coefficient (r^2) exceeds 98%, whereas it is about 90% for the North Dakota lignite. This result indicates that both analyses are consistent with each other.

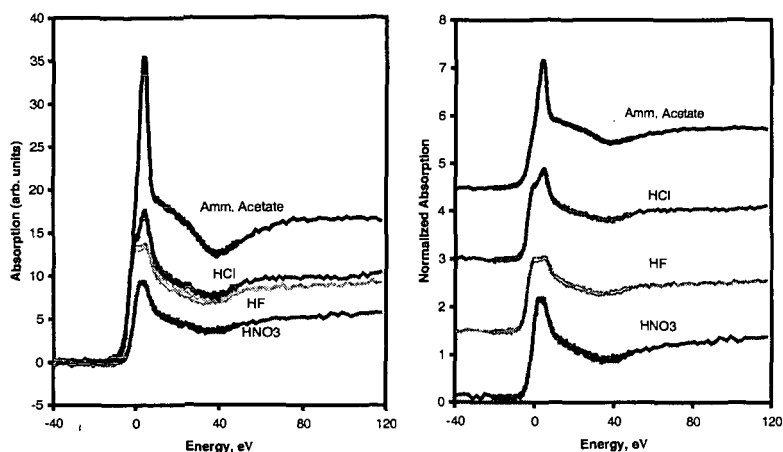


Figures 3 and 4: Unnormalized (left, Figure 3) and normalized (right, Figure 4) arsenic XANES spectra for the Ohio coal residues after different stages of the USGS leaching protocol.

(ii) XAFS Spectroscopy

Arsenic XAFS spectra were collected from the various fractions using as many as 10 scans for each sample. The spectra are shown in Figures 3 and 4 for the Ohio bituminous coal and in Figures 5 and 6 for the North Dakota lignite. Figures 3 and 5 show the unnormalized spectra, whereas Figures 4 and 6 show the same spectra normalized to the edge step and hence, these latter groupings of spectra have the effect of concentration removed from them. The data clearly show, by the reduction in intensity of the major peak at about 4.0 eV, that the HCl treatment removes principally, if not exclusively, arsenate from both the Ohio and North Dakota coals. This observation confirms more definitively the similar conclusion made in Phase 1 of this study

[4,10] based on a less direct comparison of leaching data and arsenic XAFS data for various coals. The data show also that the HF treatment has little effect, except for removing some very minor amounts of arsenate remaining after the HCl treatment. For the Ohio coal, as indicated by the reduction in intensity of the peak at about -2 eV, the HNO₃ treatment removes all of the pyritic arsenic. However, no such phase is present in the North Dakota lignite. Rather for this coal, the HNO₃ treatment appears to be removing an As³⁺ phase, as the peak that is removed is close to 0 eV. For both coals, there is a small residue of arsenic that remains after all the leachings. It is not arsenical pyrite or As³⁺, but rather more like an arsenate phase.



Figures 5 and 6: Unnormalized (left, Figure 5) and normalized (right, Figure 6) arsenic XANES spectra for North Dakota Lignite residues after different stages of the USGS leaching protocol.

A calibrated least-squares fitting model, developed earlier for quantifying arsenic species in bituminous coals [9], was used to quantify the arsenic speciation in the Ohio bituminous coal samples. For this coal, it was decided to fit only the two major arsenic forms present: arsenical pyrite and arsenate. Using this procedure [9], the arsenic speciation results obtained for the Ohio bituminous coal are summarized in Table 2. The least-squares fitting model has not yet been modified for application to the low-rank coals and their different arsenic species.

Table 2: Estimates of arsenic forms remaining after each leaching step in the Ohio coal

Leachant	%As as As/pyrite	%As as Arsenate	ppm As as As/pyrite	ppm As as Arsenate
Amm. Acetate	75	25	14.3	4.8
19.1 ppm As remains				
HCl	93	7	14.0	1.1
15.1 ppm As remains				
HF	>95	<5	>14.4	<0.8
15.2 ppm As remains				
HNO ₃	<10	>90	<0.1	>0.8
0.9 ppm As remains				

Based on this analysis, the concentration of arsenic as As/pyrite after the first three leaching steps is approximately the same, 14 ± 1 ppm. This indicates that none of the three reagents, ammonium acetate, HCl, or HF removes significant arsenic as As/pyrite. As has been postulated previously [9], the presence of arsenic in pyrite appears to make pyrite more reactive to oxidation. However, for this particular coal, it does not appear that any arsenic associated with pyrite is leached prior to the HNO₃ treatment. The HF leach appears to remove only the minor arsenate remaining after the HCl leach. The HNO₃ leach removes all of the arsenic as arsenical pyrite and appears to leave a small residue of arsenate on the carbonaceous materials. It should be noted that the arsenate in the HNO₃ residue is higher than that remaining after the HF leach, suggesting that it has been formed during the nitric acid leach.

XAFS examination of different aliquots of the two coals about a year apart shows a significant enhancement of arsenate in both coals during this time period. The arsenate species is clearly an oxidation product of other arsenic forms in the coals. Furthermore, even though the coals are not

deliberately oxidized, such oxidation is an on-going process once the coal is crushed and exposed to air. Hence, the leaching results are likely to be found to change systematically with time, reflecting this time-dependent change in arsenic speciation.

CONCLUSIONS

The use of arsenic XAFS spectroscopy to examine arsenic in leached residues of coals from a sequential leaching protocol for elemental speciation in coals has provided unparalleled insight into the leaching characteristics of arsenic from coal and enables a rather complete assessment of the assumptions behind using sequential leaching for arsenic speciation to be made. XAFS spectroscopy shows clearly that the major fraction of arsenic leached from both coals by HCl is arsenate and that HNO₃ removes much of the remaining arsenic in both coals. Leaching with HF has little effect on the arsenic content of both coals examined and appears restricted to removing any arsenate species that remains after the HCl leach. The arsenic associated with pyrite in the bituminous coal is removed effectively by nitric acid, but a quite different form is removed from the lignite by nitric acid. The XAFS data suggest that this arsenic phase may be an As³⁺ species, but it remains yet to be positively identified. Finally, a small fraction of the arsenic (5-15%) remains in the coal after the nitric acid leach. We suspect that this is an organoarsenate formed by a side reaction between the arsenic leached from the coal and new oxygen functionality on the coal introduced by reaction of the coal macerals with nitric acid.

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